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<p>Ultrathin film composite membranes consist of an ultrathin (less than 1,000 A-thickness) chemically-selective layer bonded to the surface of a microporous support membrane. Such composite membranes are important in electrochemical science because they can provide both high transport selectivity and low membrane resistance. This is possible because, while the chemically selective layer typically has high resistivity, its ultrathin nature insures that it has low resistance. We have been exploring new methods for synthesizing ultrathin film composite membranes, and we have been investigating the transport properties of the resulting composite membranes. This research effort has been extremely successful.</p>					
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**FINAL TECHNICAL REPORT**

**for Period 1 June 1990 to 31 May 1993**

**"ELECTROCHEMICAL SYNTHESIS OF ULTRATHIN FILM COMPOSITE  
MEMBRANES"**

**DTIC QUALITY INSPECTED 8**

**by**


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## FINAL TECHNICAL REPORT

This is the final report for the AFOSR-sponsored research project, "Electrochemical Synthesis of Ultrathin Film Composite Membranes." This report summarizes progress made during the period June 1, 1990 to May 31, 1993.

I. Summary. We have developed four new methods for synthesizing ultrathin film composite membranes. These methods are based on electrochemical, photochemical, redox and condensation polymerizations of ultrathin polymeric films at the surfaces of microporous support membranes. We can now make ultrathin film composite membranes based on nearly any desired polymer, including complex co- and terpolymers. This has created a tremendous opportunity for exploring the chemical, electrochemical and transport properties of thin film composites based on a wide variety of new materials. In addition, we have recently developed a new concept in electrochemical sensors--sensors based on ultrathin film composite membranes. This new concept in sensor design offers a number of advantages relative to existing sensor types. Finally, we have also developed a new approach for preparation of metal/polymer Schottky barriers based on our ultrathin film composite membranes. Hence, it is clear that the synthetic methods we are developing will have an important impact on the field of electrochemical science and technology.

II. Body. See following pages.

I. Introduction. Membranes are used in a wide variety of chemical applications including uses in electrochemical science (1) and in membrane-based separations (2). The membrane typically acts as a selective barrier, allowing some desired chemical species to pass while rejecting (or impeding transport of) other chemical species. For example, in many electrochemical applications, the membrane is asked to transport a specific ionic species (e.g.  $\text{OH}^-$  (3)) from one half-cell to another and reject all other ions. Obviously, the ideal membrane would provide **both high selectivity and high permeability**. That is, the ideal membrane would **both** discriminate very well between the desired permeant molecule and the molecules to be rejected **and** allow the desired molecule to pass unimpeded. Unfortunately, most membrane materials are far from this ideal case. Indeed, most membranes provide **either** high selectivity **or** high permeability **but not both** (see, e.g. 4-6). I call this problem the "membrane-transport Catch-22."

The chemical and/or physical basis for the membrane-transport Catch-22 varies with the type of membrane. For example, in the gas-separations membranes (4), selectivity is obtained by making the polymer glassy. However, glassy polymers show inherently low permeabilities (4) - hence the Catch-22. The bottom line is that the membrane-transport Catch-22 is a stubborn barrier to further progress in membrane science. Indeed, a recent report by the U.S. Department of Energy ranks strategies for beating this problem as one of the top priorities in the membrane research area (5). A synopsis of this DOE report was recently published in *Chemical and Engineering News*. (7).

During the previous three years of AFOSR support, we have been exploring a **general solution** to the membrane-transport Catch-22 - **ultrathin film composite membranes** (8-16). Such composites consist of an ultrathin (less than 100 nm (1,000 Å) thick) film of a chemically-selective polymer bonded to the surface of a highly-porous support membrane. The chemically-selective film provides for the desired chemical separation. This film will necessarily have low permeability, but because it is ultrathin, the net flux across this

film will be high (10). The requisite mechanical strength is provided by the support membrane; furthermore, because it is highly-porous, it too will provide high flux. Hence, in the net, the ultrathin film composite provides high chemical selectivity, high permeant flux and good mechanical strength. This combination of properties would be impossible to achieve with a homogeneous membrane (8-13).

**Our research objectives in this area have been as follows:**

1. Develop new chemical methods for preparing ultrathin film composite membranes.
2. Explore the fundamental transport properties of the resulting composite membranes.
3. Develop new chemical, electrochemical, and electronic applications of these membranes.

We have made tremendous progress in all three areas. For example, we have developed four new methods for preparing ultrathin film composite membranes (8-14). These methods are based on *interfacial polymerization* of polymer films at the surfaces of microporous support membranes. We have developed methods based on interfacial electrochemical (8,9), photochemical (10), redox (11-13), and condensation (14) polymerizations. With these methods, we can prepare ultrathin film composites based on nearly any polymer.

With regard to new applications, we have shown that such ultrathin film composite membranes can form the basis of a *new concept in sensor design* (14). In addition we have demonstrated that these composites can be used as *electrorelease membranes for large biomolecules* such as insulin (15,16). Finally, we have shown that our interfacial redox polymerization method can be used to make new metal/conductive polymer Schottky barriers (13). Progress in these various aspects of this research effort will be reviewed below.

II. Review of Scientific Accomplishments During The Previous AFOSR Contract. Research accomplishments are described in 36 research papers that have been published during the course of the contract (9-43) and in another 3 manuscripts that have been either accepted or submitted for publication (44-46).

The membrane fabrication methods we have developed are based on the concept of interfacial polymerization. Interfacial polymerization entails the synthesis of a polymer film, from the corresponding monomer(s), at the interface between the surface of the support membrane and a contacting solution or vapor phase. The key point is that because the polymerization is confined to the interface defined by the surface of the support membrane, the support membrane becomes coated with an ultrathin film of the polymer being synthesized. We have shown that this approach can be used to prepare extraordinarily-thin, defect-free films of various chemically-selective polymers (see below) at the surfaces of various types of microporous support membranes. No other thin film coating method currently approaches the power and versatility of these interfacial polymerization methods.

When the previous AFOSR contract was initiated, we had briefly described one new interfacial polymerization method in a correspondence to the *Journal of the American Chemical Society*. (8). This method is based on electrochemical polymerization of an ultrathin polymer film at the surface of a microporous membrane. We have recently written a full paper on this method (9). We have since developed three new, extremely powerful, interfacial polymerization methods. These methods are based on photochemical (10), redox (11-13), and condensation (14) polymerizations. These methods are used in the research described in this proposal. Therefore, each of these methods is briefly reviewed below.

A. Interfacial Photochemical Polymerization. We described this method in a recent paper in *Nature* (10). The microporous support membrane is placed on a filter paper that is saturated with a solution of the desired monomer(s). This solution rises to the upper surface of the membrane via capillary action and covers the membrane surface with a thin solution film. The surface is then irradiated with ultraviolet light from a Xe arc lamp to photopolymerize the monomer(s). The light strikes the membrane surface at an acute angle; this minimizes the depth of penetration of the photons thus confining the polymerization to the membrane surface. The rate of polymerization is enhanced by adding a photoinitiator (benzoin methyl ether) to the vapor phase above the membrane.

The photoinitiator induces radical polymerization (10); hence, this method is, applicable to any of the enormous number of monomers that are susceptible to this polymerization method. To illustrate this point, we have prepared ultrathin films from many different monomeric starting materials (10). Interesting (and perhaps useful) functionalized co- and terpolymers, have been prepared including electroactive and ion exchange polymers. Furthermore, this method can be used with a variety of different microporous support membranes. Finally, we have shown that this method can be used to prepare composite membranes with *defect-free films* that are as thin as 40 nm (400 Å) (10). (Our methods for proving that a film is defect-free are reviewed below.) To our knowledge, there is no other method that can produce composites with defect-free films that are this thin.

**B. Proving that a Film is Defect-Free.** If the ultrathin film that coats the support membrane surface is defective, transport across the membrane will be dominated by these defects *and chemical selectivity will be lost* (4). It is, therefore, essential that the film is defect-free. Gas-transport measurements (4,8-14) provide the ultimate test for defects in such membranes. These methods, which are used routinely in our lab, are briefly reviewed below.

Gas-transport data are obtained in a two-part cell (47). The lower half-cell is evacuated; the upper half-cell contains a known (and constant) pressure of a desired gas (e.g. O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, etc.). The membrane to be investigated separates these two half-cells. The flux of gas across the membrane is monitored via a pressure transducer in the lower half-cell. At sufficiently long times (seconds to minute depending on the film thickness), a steady-state flux across the membrane is achieved. If the rate of transport in the support membrane is much faster than the rate of transport in the ultrathin polymer film, the permeability coefficient (P) for the gas in the film can be obtained from this steady flux (8-14,39). This condition is always satisfied with our highly-permeable support membranes.

If the polymer film is defect-free, gas is transported through the polymer by a dissolution/molecular diffusion mechanism and the permeability coefficient is given by (4)

$$P = DS \quad (1)$$

where  $D$  is the diffusion coefficient and  $S$  is the Henry's law solubility coefficient for the gas in the polymer. Ideal gas-transport selectivity coefficients for the polymer can be obtained by ratioing the  $P$  values for two different gases. For example the ideal  $O_2/N_2$  gas-transport selectivity coefficient ( $\alpha_{O/N}$ ) (e.g. Figure 1) is given by

$$\alpha_{O/N} = P_O/P_N \quad (2)$$

As indicated in Equation 1, if the film is defect-free, the value of the selectivity coefficient will be dependent on the solubilities and diffusivities of the gases in the polymer.

In contrast, if *even a minute number of microscopic defects are present in the film*, gas transport across the film will be dominated by Knudsen diffusion in these defects (4). If this is the case, the selectivity coefficient for two gases in the membrane will be given by

$$\alpha_{1/2} = (MW_2/MW_1)^{1/2} \quad (3)$$

where  $MW_1$  and  $MW_2$  are the molecular weights of the gases. For  $O_2$  and  $N_2$ , this Knudsen-diffusion selectivity coefficient is 0.93.

Therefore, if the film is defect-free, the ideal gas-transport selectivity coefficient (i.e. Equations 1 and 2) will be obtained; this selectivity coefficient is typically significantly larger than the Knudsen selectivity (see below). Furthermore, one can independently determine the ideal selectivity coefficient by making measurements on thick films that are known to be defect-free (10). In contrast, if even a minute number of defects are present, the Knudsen selectivity coefficient (which can be independently calculated via Equation 3) will be obtained. It is important to clarify what is meant by "minute number of defects." Hennis and Tripodi have shown that the Knudsen selectivity coefficient will be obtained when the fraction of the film surface that is defective is only  $10^{-8}$  (4). Hence, it is clear why we assert that gas-transport measurements provide the ultimate test for defects in membranes.

We will use the following operational definition for a "defect-free" ultrathin film. If the selectivity coefficient measured for a particular ultrathin film is identical to that for a thick film that is known to be defect-free, the ultrathin film is by definition "defect-free". What this really means is that defects cannot be detected via a gas-transport measurement. However, since



this is the most sensitivity approach for probing for defects, the film will be defect-free for almost any desired application.

Finally, Table I shows O<sub>2</sub> and N<sub>2</sub> gas-transport data for a sulfonated styreneic polymer (polymer IV in Figure 4) prepared via the photopolymerization method (10). Note that the selectivity coefficients for all of the film thicknesses are identical and are almost an order of magnitude larger than the Knudsen value. Furthermore, a thick defect-free film showed the same selectivity coefficient. These data clearly show that there are "no defects" in any of these thin film composite membranes (10). This is particularly remarkable for the case of the 40 nm-thick film since this is an extraordinarily thin film.

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**Table I. Gas-Transport Properties of a Composite Membrane Based on The Sulfonated Styrenic (Polymer IV) Shown in Figure 4.**

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Film Thickness (nm)	Permeability	Coefficient*	Separation
	O <sub>2</sub>	N <sub>2</sub>	Factor O <sub>2</sub> /N <sub>2</sub>
2,300	0.54	0.066	8.2
150	0.55	0.068	8.0
40	0.57	0.071	8.0

\*In Barrers. Units are 10<sup>-10</sup> cm<sup>3</sup> (STP) cm/(cm<sup>2</sup> s cm(Hg)).

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C. Interfacial Redox Polymerization. This method is used to prepare ultrathin film composite membranes based on electronically conductive polymers (11-13). These polymers have interesting and potentially-useful electrochemical, electrochromic, and electronic properties (32). In addition, we and Kaner et al. have shown that these polymers might be potentially useful in membrane-based separations - in particular, gas separations (11,12,48). Hence, we have, as part of the AFOSR-sponsored research effort, opened a new field in the

electronically conductive polymers research area - fundamentals and applications of gas-transport in conductive polymers. I presented an invited lecture on this subject at the International Symposium on Synthetic Metals in Sweden last summer. The discussions after my lecture indicated that there is considerable interest, worldwide, in this new field.

As before, the strategy for preparation of ultrathin film composites based on conductive polymers is to create an interface that is defined by the surface of the membrane and to synthesize the conductive polymer at this interface. The polymers we have employed can be synthesized by oxidative polymerization; we have designed several interfacial polymerizations based on this chemistry (11-13). The simplest (13) begins by placing the support membrane over the opening of a vial that contains neat monomer (e.g. pyrrole, thiophene, aniline). A measured volume of an aqueous solution of the oxidizing agent (e.g.  $\text{Fe}^{3+}$ ) is applied across the upper surface of the support membrane. The oxidant solution fills the pores of the support; however, because there is no hydrostatic head, the solution does not drop into the vial containing the neat monomer. Instead, monomer vapor rises to the lower surface of the membrane where it reacts with the oxidizing agent to form a film of the corresponding polymer across this surface of the membrane (13).

Ultrathin film composite membranes based on electronically-conductive polymers have many potential applications. For example, we have shown that the synthetic method described above can be used to prepare metal/conductive polymer Schottky barriers (13). Furthermore, we have used such composite membranes to open the new field of electronically conductive polymers for membrane-based separations (11,12). Finally, these composite membranes have potential applications in electrochemical sensors and as anionically-conductive separator-membranes in electrochemical cells such as batteries.

D. Interfacial Condensation Polymerization. This method is used to prepare ultrathin film composite membranes based on siloxane polymers. The siloxanes are an extremely versatile family of polymers (49). The quintessential member of this family is poly(dimethyl-

siloxane). These polymers can be synthesized by condensation polymerization of the appropriate silane with water. For example, poly(dimethylsiloxane) can be prepared via condensation polymerization of dichlorodimethyl silane (14).

The versatility of this family of polymers stems from the ease with which other monomers can be added to the polymerization solution to impart a desired property to the resulting polymer. For example, a cross-linking monomer such as **trichloromethyl** silane can be added. Or, as we have shown (14), a cation-exchange siloxane polymer can be prepared by incorporating the monomer [2-(4-(**chlorosulfonyl**)-phenyl)ethyl] trimethoxy silane into the polymer and then *hydrolyzing the sulfonyl chloride to the sulfonic acid*. The versatility of this approach for making polymers is enhanced by the fact that an enormous number of hydrolytically unstable silanes are commercially available.

The siloxane polymers have another important attribute that is particularly useful in applications that involve transport. The parent polymer (poly(dimethylsiloxane)) has a glass-transition temperature ( $T_g$ ) of  $-127^\circ\text{C}$  (50). This extraordinarily-low  $T_g$  insures that molecular fluxes across films of such polymers will be high. Indeed, because of this low  $T_g$ , even large organic molecules show appreciable fluxes through such polymers (51). While derivatization of the parent polymer, for example with ionic groups (14), will clearly raise the  $T_g$  somewhat, this family of polymers can, in general, be viewed as a *class of high permeant-flux, but low permeant-selectivity, materials*. As we will see, these can be very useful attributes.

The method that we have developed for forming ultrathin film composite membranes via condensation polymerization of siloxane polymers (14) is identical to the interfacial redox polymerization method except that pure water replaces the oxidant solution. We have shown that this method can be used to form defect-free films that are as thin as 50 nm (14). We have also shown that siloxane polymer films of this type can be chemically derivatized *after film formation* by exposing the polymer film to a solution of a desired hydrolytically-unstable silane (14). This results in chemical attachment of the desired silane to the chain ends of the

siloxane polymer. This approach works because the siloxane chains end in -OH and thus act as sites for attachment of hydrolytically-unstable silanes.

These siloxane polymer-based composites have a number of potential applications. For example, we have shown that these membranes can form the basis of a new concept in sensor design (14). The key advantages of this new sensor design are fast response (because the device is based on an ultrathin film) and versatility (it should be applicable to nearly any molecular-recognition chemistry and any signal-transduction method). To demonstrate this new sensor concept, we prepared and evaluated a prototype electrochemical glucose sensor (14). This sensor produced a linear response to glucose over the physiologically-important concentration range. Furthermore, the response time was, indeed, fast - less than 2 seconds. We believe that this might be a useful concept for the design of future generations of chemical sensors.

III. Conclusions. The research effort during the previous three years of AFOSR support has led to the development of new methods for preparing ultrathin film composite membranes and new applications of such membranes. The objectives of the research effort, as spelled out in the AFOSR proposal, were accomplished.

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III. Status of Research. Completed.

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## **V. Participating Professionals.**

1. George J. Collins
2. A. Clearfield
3. Harry R. Allcock

### **A. Post docs, graduate students and other collaborators:**

1. Marjorie Nicholson
2. Chao Liu
3. Scott Stowe
4. Jorge L. Colón
5. Leon Van Dyke
6. Del R. Lawson
7. Charles J. Brumlik
8. Wen-Janq Chen
9. Wenbin Liang
10. Barbara Ballarin
11. Elizabeth Luebker
12. J. A. Dodge
13. Z. Yu
14. C.-Y. Yang
15. Venod Menon
16. Ranjani Parthasarathy
17. Daniel L. Feldheim
18. Arvind Parthasarathy
19. D. S. Thakur
20. M. J. Tierney
21. M. W. Espenscheid
22. Junting Lei

### **B. Degrees Granted:**

1. Majorie A. Nicholson, M. S., "Effect of Polymer Electrode Morphology on Performance of a Lithium/Polypyrrole Battery," May 1991.
2. Chao Liu, Ph. D., "Development of High-Performance Composite Membranes for Electrochemical Processes and Gas Separations," September 1991.
3. Zhihua Cai, Ph. D., "Synthesis and Characterization of Electronically Conductive Heterocyclic Polymers," September 1991.
4. Junting Lei, Ph. D., "Investigations of the Chemical and Electronic Properties of Polypyrrole and its Derivatives," January 1992.
5. Arvind Parthasarathy, "Oxygen Reduction at the Platinum/Nafion Interface: Electrode Kinetics and Mass Transport," December 1992.

V. Interactions. Lectures presented:

1. "Template Synthesis of Electronically Conductive Polymers," International Society of Electrochemistry, Berlin, GERMANY, September 5-10, 1993
1. "Nanomaterials," National Renewable Energy Laboratory, Golden, Colorado, August 18, 1993.
2. "Membrane-based Separations with Electronically Conductive Polymers," Gordon Conference on Membranes: Materials and Processes, Plymouth State College, New Hampshire, August 1-6, 1993.
3. "Nanochemistry--A Membrane-Based Approach," University of Cincinnati, Cincinnati, Ohio, July 29, 1993.
4. "Nanochemistry--A Membrane-Based Approach," University of Arizona, Tucson, Arizona, May 5, 1993.
5. "Template Synthesis of Electronically Conductive Polymers - A New Route for Achieving Higher Electronic Conductivities," Electrochemical Society meeting, Honolulu, Hawaii, May 16-21, 1993.
6. "Chemical Sensors Based on Ultrathin Film Composite Membranes - A New Concept in Sensor Design," Electrochemical Society meeting, Honolulu, Hawaii, May 16-21, 1993.
7. "Solid-State Electrochemistry--Electrochemical Measurement of Oxygen Transport in Nafion Membranes in the Absence of a Contacting Electrolyte Phase," Electrochemical Society meeting, Honolulu, Hawaii, May 16-21, 1993.
8. "Template Synthesis of Electronically Conductive Polymers - A New Route for Achieving Higher Electronic Conductivities," International Union of Pure and Applied Chemistry Commission meeting, Honolulu, Hawaii, May 15, 1993.
9. "Bioencapsulation in Electronically Conductive Polymer Nanotubules," American Chemical Society meeting, Denver, Colorado, April 1, 1993.
10. "Electrochemical Investigations of the Nafion/Platinum Interface Using a Solid-State Electrochemical Cell," American Chemical Society meeting, Denver, Colorado, March 30, 1993.
11. "Biosensors Based on Ultrathin Film Composite Membranes," American Chemical Society meeting, Denver, Colorado, March 29, 1993.
12. "New Ideas in Biosensors and Biocatalysis," Gordon Conference on Bioanalytical Sensors, Ventura, California, March 22-26, 1993.
13. "Concerted Ion and Electron Transfer Across Electronically Conductive Polymer Membranes," Materials Research Society meeting, Pittsburgh, Pennsylvania, December 1, 1992.

14. "Template Synthesis - A Method for Enhancing Supramolecular Order in Electronically Conductive Polymers," Materials Research Society meeting, Pittsburgh, Pennsylvania, December 2, 1992.
15. "Synthesis, Characterization and Electronic Properties of Electronically Conductive Polymer Microstructures," Oregon Graduate Institute of Science and Technology, Beaverton, Oregon, October 2, 1992.
16. "Electronically Conductive Polymers as Chemically Selective Layers for Membrane-Based Separations," International Conference on Science and Technology of Synthetic Metals, Gothenburg, SWEDEN, August 16, 1992.
17. "New Ideas in Biosensors and Biocatalysis," Anna University, Madras, INDIA, August 12, 1992.
18. "Electronically Conductive Polymer Microstructures--Tubules, Fibrils and Ultrathin Films," SPIC Science Foundation, Madras, INDIA, August 10, 1992.
19. "Template Synthesis of Electronically Conductive Polymers--A New Route for Achieving Higher Electronic Conductivities," University of Rome, Rome, ITALY, July 30, 1992.
20. "New Ideas in Biosensors and Biocatalysis" University of Venice, Venice, ITALY, July 27, 1992.
21. "Template Synthesis of Electronically Conductive Polymers--A New Route for Achieving Higher Electronic Conductivities," University of Ulm, Ulm, GERMANY, July 23, 1992.
22. "Ultrathin Film Composite Membranes for Gas Separations," Materials Research Society Spring '92 meeting, San Francisco, California, April 27-May 2, 1992.
23. "Template Synthesis of Polymeric Micro and Nano Structures: Tubules, Fibrils and Ultrathin Films," California Institute of Technology, Pasadena, California, April 23-24, 1992.
24. "Biosensors Based on Ultrathin Film Composite Membranes," American Chemical Society Meeting, San Francisco, California, April 5-10, 1992.
25. "Electronically Conductive Polymer Microstructures--Tubules, Fibers and Ultrathin Films," University of New Mexico, Albuquerque, New Mexico, April 3, 1992.
26. "Electronically Conductive Polymer Microstructures--Tubules, Fibers and Ultrathin Films," University of Southern Mississippi, Hattiesburg, Mississippi, March 31, 1992.
27. "Plasma Polymerization of Perfluorinated Ionomer Membranes for Solid Polymer Electrolyte Fuel Cells," University of Colorado Center for Separations Using Thin Films, Boulder, Colorado, January 27-28, 1992.

28. "Ultrathin Film Composite Hollow Fibers for Pervaporation Separations," University of Colorado Center for Separations Using Thin Films, Boulder, Colorado, January 27-28, 1992.
29. "Electronically Conductive Polymers--New Plastics that Conduct Electricity Like Metals," Regis College, Denver, Colorado, November 9, 1992.
30. "Ultrathin Film Composite Membrane-Based Sensors--A New Concept in Sensor Design," Jet Propulsion Laboratory, Pasadena, California, November 7, 1991.
31. "Template-Synthesis of Conductive Polymers--Enhanced Electronic Conductivity, Enhanced Supermolecular Order and Interesting Microstructures," Naval Weapons Center, China Lake, California, November 5, 1991.
32. "Conductive Polymer Microstructures--Tubules, Fibrils and Ultrathin Films," University of California at Los Angeles, Los Angeles, California, October 8, 1991.
33. "Conductive Polymer Microstructures--Tubules, Fibrils and Ultrathin Films," University of California at San Diego, San Diego, California, October 10, 1991.
34. "Conductive Polymer Microstructures--Tubules, Fibrils and Ultrathin Films," Harvey Mudd College, Claremont, California, October 7, 1991.
35. "Conductive Polymer Microstructures--Tubules, Fibrils and Ultrathin Films," Occidental College, Los Angeles, California, October 8, 1991.
36. "New Ultrathin Film Composite Membranes for Gas Separations," Air Products and Chemicals, Allentown, Pennsylvania, July 9, 1991.
37. "Template Synthesis of Electronically Conductive Polymers," Allied-Signal Inc., Morristown, New Jersey, July 8, 1991.
38. "Template Synthesis of Electronically Conductive Polymers," Third International Symposium on Solid Polymer Electrolytes, Annecy, France, June 19, 1991.
39. "Ultrathin Film Composite Membranes for Sensor Applications," ACS Meeting, Atlanta, Georgia, April 17, 1991.
40. "Template-Synthesis of Conductive Polymers - Enhanced Electronic Conductivity, Enhanced Supermolecular Order and Interesting Microstructures," ACS Meeting, Atlanta, Georgia, April 17, 1991.
41. "Ultrathin Film Composite Membranes," Dow Chemical Company, Midland, Michigan, April 8, 1991.
42. "Ultrathin Film Composite Membranes for Gas Separations," Los Alamos National Labs, Los Alamos, New Mexico, March 11, 1991.
43. "Electronically Conductive Polymers - New Plastics that Conduct Electricity Like Metals," Sigma Xi, Colorado State University, Ft. Collins, Colorado, February 22,

1991.

44. "Enhancing Conductivities in Electronically Conductive Polymers," University of Kansas, Lawrence, Kansas, February 4, 1991.
45. "Template Synthesis of Electronically Conductive Polymers," University of Wyoming, Laramie, Wyoming, December 4, 1990.
46. "Enhancing Conductivities in Electronically Conductive Polymers," Solar Energy Research Institute, Golden, Colorado, October 19, 1990.
47. "Enhancing the Conductivities of Electronically Conductive Polymers," University of Colorado, Boulder, Colorado, September 18, 1990.
48. "Enhancing the Conductivities of Electronically Conductive Polymers," Iowa State University, Ames, Iowa, September 7, 1990.
49. "Ultramicroelectrodes and Transparent Metal Films," Iowa State University, Ames, Iowa, September 6, 1990.
50. "Enhancing the Conductivities of Electronically Conductive Polymers," Rocky Mountain Conference, Denver, Colorado, July 30, 1990.

VII. New Discoveries. A new concept in sensor design was developed. This concept is based on the ultrathin film composite membranes that are the topic of this research effort.

VIII. Statement for Program Manager. We have developed four new methods for synthesis of ultrathin film composite membranes. These methods allow for membranes to be prepared that have almost any chemical composition.